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(54) Title: THIN LAYER CATALYST TO ADHERE TO A METALLIC SUBSTRATE AND METHOD OF FORMING THE SAME

(57) Abstract: A method of forming a catalyst coating on a metallic surface is disclosed. The method comprises: mixing non-dispersible catalyst particles with water and a dispersible solid to form a washcoat; adjusting the pH of the washcoat to produce a predetermine viscosity; coating the washcoat onto a metallic surface; and drying and calcining the coating. A catalyst coating for application to a metal surface and a steam reformer and a fuel cell with catalyst coatings applied by the above method are also disclosed.

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THIN LAYER CATALYST TO ADHERE TO A METALLIC SUBSTRATE AND METHOD OF FORMING THE SAME

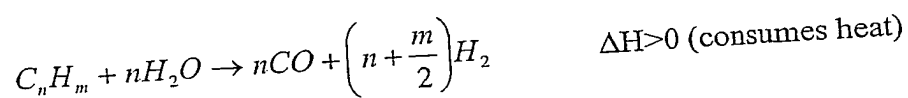
Background

This invention relates to a catalyst which can be formed into a thin layer comprising catalytically active components dispersed within a support which is particularly suitable for application to metallic components.

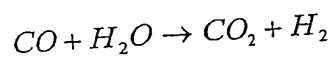
As is well known in the art, catalysts increase the rate of a chemical reaction without suffering any permanent chemical change themselves.

Catalysts are used in the so-called "Steam Reforming" process for the conversion of hydrocarbon fuels into hydrogen. The hydrogen produced can be purified for general use or used as a feedstock for chemical processes such as methanol or ammonia production. The hydrogen is particularly suitable for use in fuel cell systems, where conversion of hydrocarbons to hydrogen facilitates the generation of electrical power.

Conventionally, hydrocarbons can be converted into hydrogen by steam reforming:



This reaction is always accompanied by partial conversion of the carbon monoxide product via the shift reaction:



The steam reforming reaction is of great importance industrially, being one of the most widely used means of converting fossil fuels to hydrogen. The product gas composition is determined by the thermodynamics of the system and can be influenced via the reactant ratios, temperature and pressure. However, in order to obtain a useful reaction rate, the reaction is carried out at high temperature and pressure, frequently using a nickel catalyst. Crucially, the reaction is endothermic i.e. it consumes heat. Consequently, heat must be added to reactors in order to support the reaction. It is the need to supply this heat efficiently that determines reactor designs – the more rapidly heat can be added, the higher the throughput possible.

Conventional reactor designs utilise a reaction chamber packed with catalyst to perform the steam reforming reaction. The reaction chamber is in good thermal contact with a second vessel, which may be a furnace surrounding the first chamber to provide heat to drive the steam reforming reaction in favour of hydrogen. Such a reactor is disclosed in US 4203950. Importantly, the catalyst is normally in the form of particles, typically at least 3mm equant cylinders, in order to provide a stable packed bed of catalyst and a degree of voidage, so favouring a small pressure drop between reactor inlet and outlet. The CRG family of catalysts originally developed for the CRG process (see GB 820257) by British Gas are an example of such a catalyst type and have been shown to be stable, active and particularly suitable for the harsh environments within certain fuel cells.

Another type of steam reformer is a Haldor Topsoe Heat Exchange Reformer as described in 'Scale up Study of Heat Exchange Reformer for 5MW Fuel Cell Plant' from the 1992 Fuel Cell Seminar Proceedings, Courtesy Associates Inc., Washington DC, USA. This reformer has a toroidal-shaped catalyst bed acting as the first reaction chamber with heat from a burner supplied to the inside and outside of the toroid. The application of heat to both the inside and outside of the toroidal shaped catalyst bed improves the heat transfer to the first reaction chamber and so also the energy density of the reformer when used to supply hydrogen to a fuel cell.

A further type of steam reformer is an IHI plate reformer as described in EP-A-0430184. This reformer includes a multi-layer unit comprised of parallel plates that are welded together to form a series of chambers. Alternating chambers are used for steam reforming and for combustion which improves the heat transfer between the combustion region and the steam reforming region and so also the energy density of this type of reformer when used with a fuel cell.

However, such reactors are generally large and heavy because of their need to house solid catalyst particles and/or because of their brazed or welded construction. The reactors are particularly unsuitable for use in mobile applications such as to provide hydrogen to one or more fuel cells in a vehicle. Furthermore it is desirable to improve the heat transfer between the first and second regions of such reactors, since the heat transfer characteristics of catalyst beds are inherently poor. State-of-the-art reactors, which

overcome these difficulties, are disclosed in WO 01/10773 and WO 98/33587 and are known as Advantica Compact Reformers. These reactors use compact heat exchangers to pass heat between exothermic combustion reactions and endothermic steam reforming reactions. Crucially, the catalyst is in the form of thin layers coated directly on either side of the heat exchange surface using a sol gel. Thus heat is released or consumed exactly where it needs to be in order to facilitate good heat transfer – at the heat exchange surface. Such reactors are capable of performance equivalent to conventional reactors 1-2 orders of magnitude larger.

The thin layer catalyst embodied in the current invention is particularly applicable to this type of reactor. The thin layer reduces the length of diffusion paths and results in a catalyst of higher apparent activity than pellets. The hydrogen produced, with appropriate purification, is particularly suitable for use in fuel cells such as phosphoric acid fuel cells (PAFC), alkaline fuel cells (AFC) or the solid polymer type, otherwise known as proton exchange membrane or polymer electrolyte membrane (PEM) fuel cells. The fuel cell types mentioned above are generally regarded as low temperature fuel cells.

There are fuel cell types which operate at sufficiently high temperatures to support useful rates of reaction from steam reforming catalysts without the use of a separately heated reactor. Molten carbonate fuel cells (MCFC) operate at approximately 650°C. These

benefit from the placement of reformers in good thermal contact with the fuel cell stack so that waste heat can be used to supply the reforming enthalpy rather than combusting additional fuel. This approach is known as indirect internal reforming (IIR) and results in efficient systems, not only because waste heat may be used to drive the steam reforming reaction, but also because the systems have a lower requirement for fuel cell cooling. Alternatively, steam reforming catalyst may be inserted into the gas distribution channels of the fuel cells, where thermal contact is at its greatest and where the consumption of hydrogen by the fuel cells drives the steam reforming reaction further towards completion, aiding high efficiency further. This approach is known as direct internal reforming (DIR).

The present invention is applicable to these systems too. Application of the catalyst to the metallic components within the MCFC stack offers the benefit of less catalyst needed (because the activity is higher) than would be the case with conventional catalyst forms and lower pressure drop within the gas distribution channels. The catalyst can be applied either to the fuel cell separator plates or to the porous anode itself. Furthermore, certain of the CRG catalysts have proven endurance in the harsh molten carbonate-containing environment within the MCFC stack.

A further type of fuel cell is the solid oxide fuel cell (SOFC). Conventionally, this operates at 800-1000°C. At these temperatures, the nickel containing anode material

possesses ample activity to fuel the cell without insertion of dedicated steam reforming catalyst. However, lower temperature variants are currently being developed. Developers are driven by the need to avoid relatively expensive temperature resistant materials. Thus, low temperature SOFCs are likely to operate at 650°C or less, utilise metallic components and require steam reforming catalyst, a similar scenario to that of current MCFCs. Consequently, the current invention is applicable to low temperature SOFCs where it provides identical benefits to those conferred on MCFCs.

SOFCs operating at conventional temperatures frequently require partial steam reforming of fuel before it can be used to fuel the cells directly. This is known as pre-reforming and is carried out to remove relatively high molecular weight hydrocarbons and reduce the enthalpy requirement of the fuel/steam mixture. Thus pre-reforming avoids the use of large quantities of steam, which would otherwise be necessary to prevent harmful side reactions. Also, the precipitous drop in temperature caused at the cell inlets by the steam reforming reaction is reduced, mitigating the threat of thermal shock to the delicate ceramic cells and avoiding inefficient areas of cells. The current invention is applicable in pre-reformers also, where the active catalyst offers the opportunity to reduce reactor size, and where efficient heat transfer allows achievement of methane conversions not realistic with adiabatic reactors.

However, it has been found to be difficult to produce catalyst in a form with suitable fluid properties to be able to be applied as a coating with sufficient catalytic activity and with the ability to adhere to metallic surfaces, such as in steam reformers and fuel cells.

The present invention seeks to alleviate these problems by producing catalyst in a form with satisfactory fluid properties to enable it to be applied as a coating with sufficient catalytic activity and with sufficient adhesion properties to enable it to adhere to a metal surface.

According to a first aspect of the present invention, there is provided a method of forming a catalyst coating on a metallic surface, the method comprising:-

mixing non-dispersible catalyst particles with water and a water dispersible solid to form a washcoat;

adjusting the pH of the mixture to produce a predetermined viscosity;

coating the mixture onto a metallic surface; and

drying and calcining the coating.

Such a method enables active catalyst to adhere to a metallic substrate such as stainless steel. The use of a washcoat rather than other fluids such as a sol gel for example produces a far more effective catalytic layer as a washcoat is thicker and contains more

catalyst and so does not require the deposition of multiple layers reducing the likelihood of faults and reducing production time and costs.

The water dispersible solid may be an oxide such as alumina or ceria.

The pH of the mixture is selected according to a function relating pH and viscosity to ensure satisfactory fluid properties to enable the mixture to be coated onto a desired metallic surface.

The non-dispersible catalyst particles are preferably between 1 μ m and 100 μ m in size. The metallic surface is preferably prepared prior to being coated by being roughened, by abrasion or by being etched, for example, to enable the catalyst coating to key into the surface. The metallic surface is preferably cleaned. Roughening the surface area and cleaning increases the ability of the coating to adhere to the metallic surface. The metallic surface to which the catalyst coating is applied may be a wall of a steam reformer or a fuel cell.

According to a second aspect of the present invention, there is provided a catalyst for application as a layer to a metallic surface, the catalyst being provided as non-dispersible particles in a solution of water dispersible solid for application as a washcoat.

According to a third aspect of the present invention, there is provided a metallic surface with a catalyst coating applied according to the first aspect of the present invention. The metallic surface may form part of a steam reformer or a fuel cell.

An example of the present invention will now be described with reference to the accompanying drawings, in which:-

Figure 1 shows a function showing the relationship between pH and viscosity of a coating;

Figure 2 shows the structure of a catalyst layer applied to a metallic surface; and

Figure 3 shows an MCFC system.

The catalyst is applied by washcoat technology. Washcoat technology utilises a water-dispersible solid mixed with a larger-particle non-dispersible solid (the passenger) to form a layer consisting of a suspension of non-dispersible solid catalyst passenger particles bound together in a matrix or solution. The steam reforming catalyst may be applied as a thin layer of washcoat. In the present example, reforming catalyst pellets ground to a small particle size typically between 1 and 100 μm form the passenger.

The use of a washcoat with the presence of relatively large non-dispersible catalyst particles (e.g. between 1 and 100 μm) provides more catalyst than a sol gel coating which would be much thinner and only has dispersible solid particles of a much smaller size of a few nanometres than the non-dispersible particles of a washcoat.

The catalyst is applied to a substrate as a washcoat. 5-20g of water-dispersible alumina (such as classic 'Disperal' or P2 grade) are added to 100ml of deionised water. Dispersion of this material is facilitated by vigorous agitation with a high shear rate homogeniser as the material is added to the water. After the alumina is fully dispersed, 10-50g of LH catalyst (as is well known in the art available from Syntex and as described in GB 2222963 and GB 2295920) is added and dispersed similarly.

The coating must be applied at a suitable pH in order for the mixture to possess the necessary viscosity. The pH and viscosity of the coating are inter-related as shown by the graph of Figure 1. The pH of the coating is adjusted to enable it to produce the viscosity for successful coating on the desired metallic surface. Acidification is achieved by the dropwise addition of 69% concentrated nitric acid while agitating with a high shear rate homogeniser. After the acid has been added and dispersed, the homogenizer is turned off and the washcoat left to stand for between 10 and 15 minutes before the coating is made. Optimal coatings are achieved for the channels of a so-called Advantica compact reformer (see WO 98/33587) when the coating is applied between pH 3 and 8.5. However, different viscosities and thus different pHs will be required for different applications. An advantage of the present invention is that the viscosity can be controlled to predetermined level by manipulation of the pH of the coating.

The coatings can be applied to metallic substrates, particularly metals of the stainless steel type, such as 316L and high temperature alloys such as Nicrofer 3220H. It is

advantageous to prepare the substrate to receive the coating, generally by roughening it. This can be achieved, for example, by abrasion (e.g. with 60 grit emery paper) or by etching with standard etchants such as ferric chloride. The surface of the substrate is treated to make it exceptionally clean. This is achieved by cleaning in an ultrasonic bath using an aqueous solution of detergent followed by drying in air and cleaning further in an ultrasonic bath using dichloromethane.

Application of the coating can be achieved in various ways. The substrate can be dipped in the washcoat mixture. In this case, the speed of removal of the piece from the washcoat mixture influences the thickness of the catalyst layer since the mixture viscosity depends on the shear rate. Alternatively, the mixture can be sprayed onto the substrate. This is a particularly suitable application method for porous substrates, such as MCFC anodes, which will tend to absorb catalyst mixture. In this case, spraying is facilitated by using a mixture of somewhat lower viscosity, by adjusting the pH appropriately. When applying the coatings to compact heat exchangers, there is a danger of formation of air locks within the intricate internal structure. This would cause uncatalysed areas, which would increase the danger of forming damaging hot spots. In this case, the coating is formed by first evacuating the heat exchanger and then allowing the vacuum to draw catalyst mixture into the heat exchanger, completely filling it. By passing air through the heat exchanger, excess catalyst is then expelled. The pressure applied exerts a degree of control of the catalyst loading achieved.

Regardless of the method of applying the coating and the nature of the substrate, the catalyst layer must be dried before calcining. This is achieved in air at ambient or near ambient temperature. In the case of the compact heat exchanger, this is facilitated by passing a low flow rate of air through the heat exchanger.

Calcining of the catalyst is achieved by heating to 600°C in air, gradually increasing the temperature by less than 5°C per minute, preferably 2°C or less per minute and holding at that temperature for 30 minutes. The temperature is increased at this relatively slow rate to remove any remaining water slowly. If water is removed too quickly, it could cause damage to the coating and affect its adhesion.

The catalyst layer formed by the above method is shown in Figure 2. It consists of a thin layer of conventional steam-reforming catalyst composition 2 with particles of an average size between 1 and 100 µm embedded in a microporous alumina matrix 3 adherent to the metallic substrate 1.

Alternatively the matrix can be ceria. This has the advantage that unlike alumina, it forms no solid solution with nickel so that all the nickel is potentially available for catalysis. However, ceria does have the disadvantage that it is an intrinsically low surface area support.

The majority of the catalyst material when provided in conventional catalyst pellets is unused. This is because finite diffusion of reactant gases means that reaction is complete long before gases have diffused to the centre of the pellets. The smaller diffusion paths associated with the thin layer of small catalyst particles means that the in the present invention higher reaction rates are achievable. This is manifested as a higher apparent catalyst activity. For example, utilising a catalyst of the CRG family designated LH, the reaction rate increases over that obtained from conventional particles by a factor of 12.8 when applied to a stainless steel substrate by washcoat methods (see Table 1).

Table 1. Reaction Rate Gain Associated with Thin Layers (LH catalyst)

Catalyst form	Pellet	Layer
Dimensions	3.1mm equant cylinder	0.02mm layer
1 st order rate constant (mmol/s/g/bar)	3.2	41

Examples

The benefits of the current invention are described above in the introduction. The catalyst described, being an extremely active catalyst adherent upon stainless steel substrates, is a key enabling technology for several fuel cell types. The benefits can be illustrated by the several examples below.

Example 1 – Used Within an Advantica Compact Steam Reformer

The conditions illustrated in Table 2 can be applied to a compact reactor containing LH catalyst. The volume of the reformer required to fuel a 200kW_e PEM system is then given in Table 3. This shows that much smaller reactors are possible using a compact heat exchanger and thin-film catalysts. Furthermore, if the thin-film variant of LH catalyst is replaced by catalyst pellets, a reactor at least twice the size results.

Table 2. Compact Reactor Conditions Used in Example 1

	Reforming side	Combustion side
Feed temperature (°C)	650	650
Pressure (bara)	3	1
Natural gas feed rate (kmol/hr)	1.7	0.5
Steam feed rate (kmol/hr)	5.2	N/A
Air feed rate (kmol/hr)	N/A	5.2

Table 3. Volume of Reactors Needed to Supply Hydrogen to a 200kW_e PEM

	Reactor size (litres)
Haldor Topsoe Heat Exchange Reformer	2000
IHI Plate Reformer	666
Hybrid reactor utilising 3mm equant LH pellets	>27
Compact Reactor Utilising LH catalyst according to the present invention	13.5

Example 2 – Catalysed DIR-MCFC Hardware

A simplified, highly efficient MCFC system is shown in Figure 3. This system can be operated using the conditions shown in Table 4. As shown in Table 5, when this system is operated with 5kg of LH catalyst pellets within the gas distribution channels, a high methane conversion and system efficiency result. However, the particular attributes of the current invention mean that the catalyst loading can be reduced by a factor of around 8 without loss of performance.

Table 4. Operating Conditions used in Example 2

Anode inlet temperature (°C)	630
Anode outlet temperature (°C)	670
Methane preheat temperature (°C)	350
Anode recycle ratio	0.48
Cathode recycle ratio	0.67
Methane feed rate (kmol/hr)	1.56

Table 5. Performance of MCFC System with LH Catalyst of Different Form

	3.2 mm catalyst pellets	Thin film
Gross electrical efficiency (%)	57.7	57.4
Cathode air requirement (kmol/hr)	6.0	6.1
Methane conversion (%)	97.5	97.5
Catalyst loading required (g/m ²)	5000	620

Example 3 – Pre-Reformer in an SOFC

The operating conditions shown in Table 6 are appropriate for a planar SOFC without anode recycle. Using these conditions, a prereformer operating adiabatically with heat exchange from anode off-gas supplying pre-heat could give a maximum of 16% methane conversion (see Table 6). However, the thin layer catalyst described above enables the heat exchange and reforming functions to be integrated into a compact heat exchanger, allowing conversions of up to 26%. Furthermore, the thin film catalyst also enables the use of a compact reactor of the type disclosed in WO 0110773 and WO 9833587 to be used to integrate the anode off-gas burner into the assembly also. Now methane conversions up to 45% are possible. Thus, the thin film catalyst extends the range of methane conversions obtainable from SOFC prereformers, while simplifying the process design.

Table 6. Operating Conditions used in Example 3

Stack outlet temperature (°C)	900
System pressure (bara)	1
Stack inlet steam:carbon ratio	2
Fuel utilization (%)	90

Table 7. Performance of Prereforming Options in an SOFC

	Reactor exhaust temperature (°C)	Methane conversion (%)
Conventional adiabatic reactor	401	16
Compact heat exchanger with thin-film catalyst	462	26
Compact Reformer	540	45

Claims

1. A method of forming a catalyst coating on a metallic surface, the method comprising:-
 - mixing non-dispersible catalyst particles with water and a water dispersible solid to form a washcoat;
 - adjusting the pH of the mixture to produce a predetermined viscosity;
 - coating the mixture onto a metallic surface;
 - drying and calcining the coating.
2. A method according to claim 1, wherein the water dispersible solid is an oxide.
3. A method according to claim 2, wherein the water dispersible oxide is alumina.
4. A method according to claim 2, wherein the water dispersible oxide is ceria.
5. A method according to claim 1, wherein the catalyst particles have an average diameter between 1 μm and 100 μm .
6. A method according to claim 5, wherein the catalyst particles are produced by grinding catalyst pellets.

7. A method according to any of the preceding claims in which the metallic surface upon which the catalyst is coated is roughened prior to coating.
8. A method according to claim 7, wherein the metallic surface is roughened by abrasion.
9. A method according to claim 7, wherein the metallic surface is roughened by being etched.
10. A method according to any of claims 7 to 9, wherein the metallic surface is cleaned after roughening.
11. A method according to any of the preceding claims, wherein calcining of the coating is achieved by gradually increasing the temperature of the coating at less than 5°C per minute.
12. A method according to claim 11, wherein calcining of the coating is achieved by gradually increasing the temperature of the coating at less than 2°C per minute.
13. A method according to any one of the preceding claims, in which the metallic surface to be coated is a channel forming part of a heat exchanger, steam reformer or fuel

cell and the coating process includes evacuating air from the channel, allowing the vacuum to draw catalyst mixture into the channel completely filling it and then passing a gas through the channel to expel excess catalyst.

14. A method according to claim 13, wherein the pressure of gas passed through the channel to expel excess catalyst is predetermined to control the catalyst loading achieved.

15. A method substantially as hereinbefore described with reference to the accompanying drawings.

16. A catalyst for application as a coating to a metallic surface, the catalyst being provided as non-dispersible particles in a water dispersible solid solution to form a washcoat.

17. A catalyst according to claim 16, in which the non-dispersible catalyst particles have an average diameter between 1 μm and 100 μm .

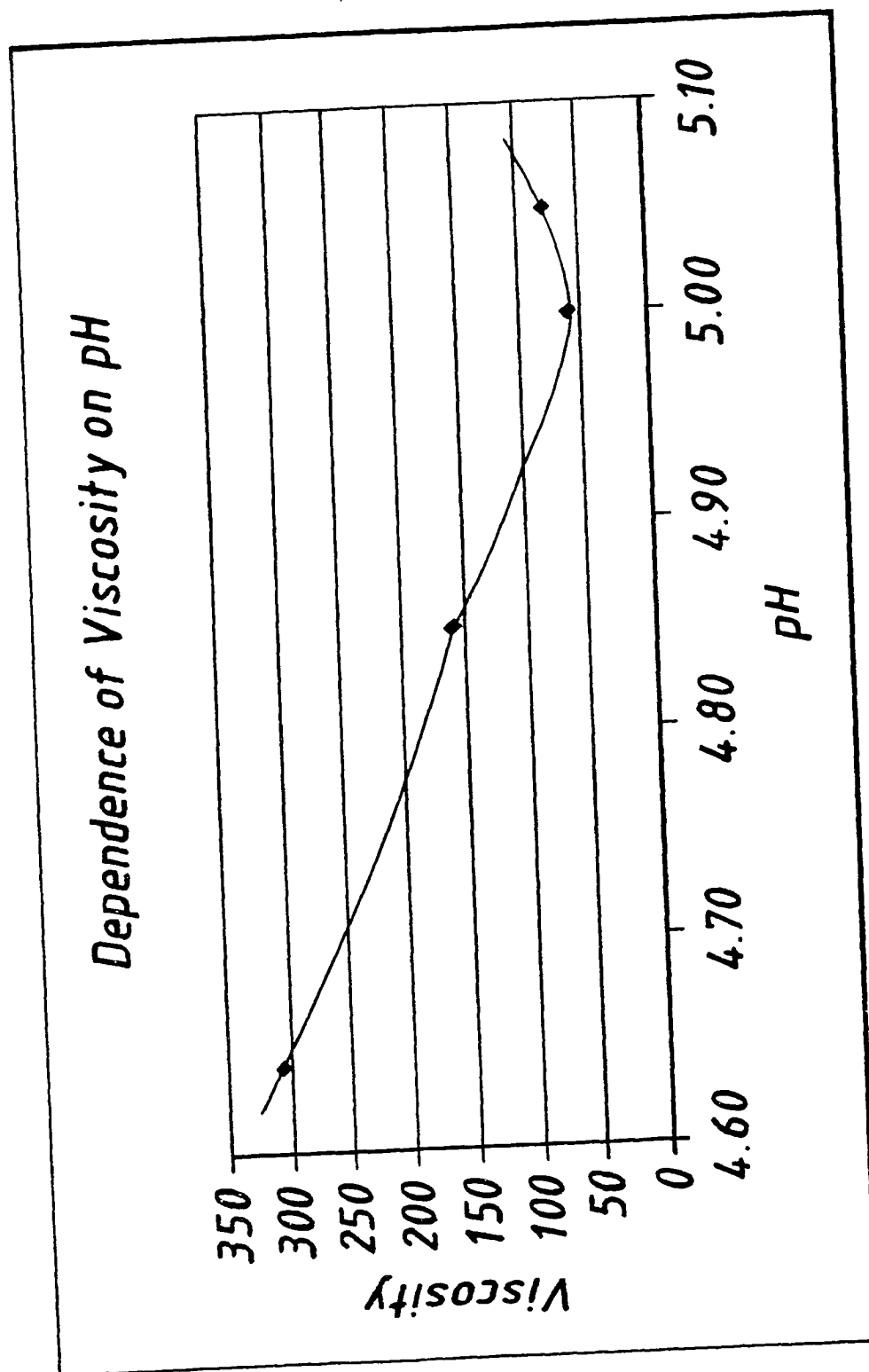
18. A catalyst according to claim 16 or claim 17, having a pH between 3 and 8.5.

19. A catalyst as hereinbefore described with reference to the accompanying drawings.

20. A metallic surface with a catalyst coating applied according to the method of any of claims 1 to 15.
21. A steam reformer including a metallic surface according to claim 20.
22. A fuel cell including a metallic surface according to claim 20.

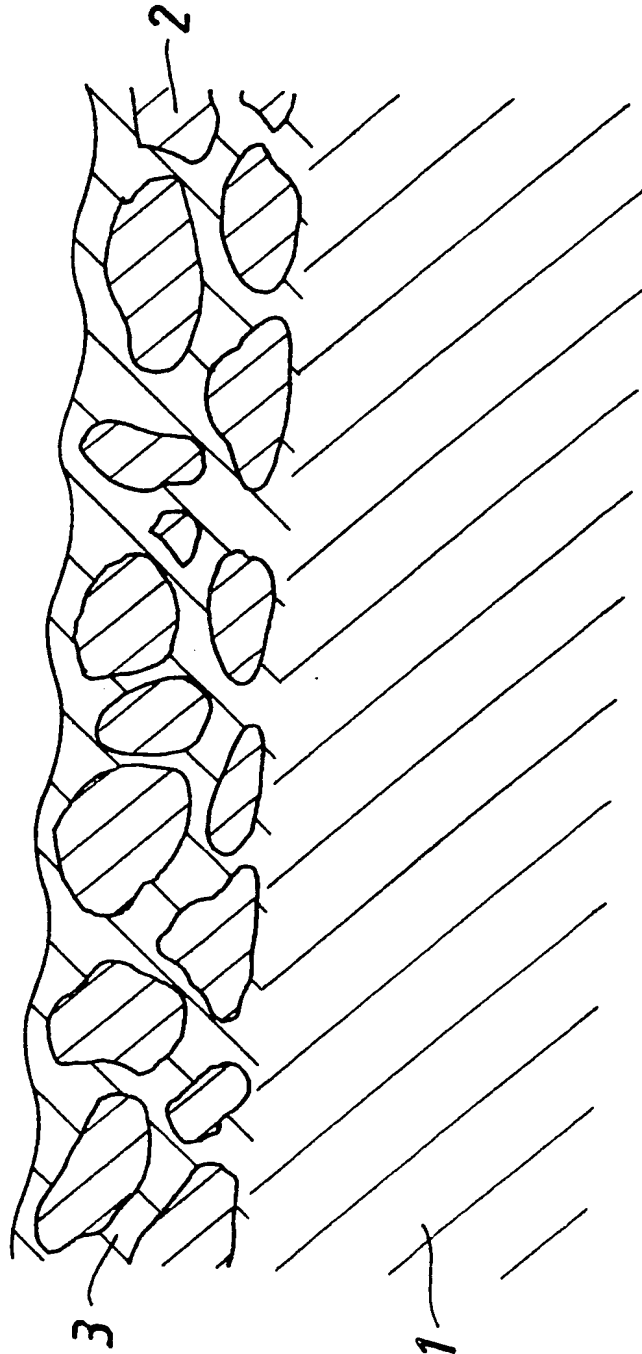
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FIG.1.



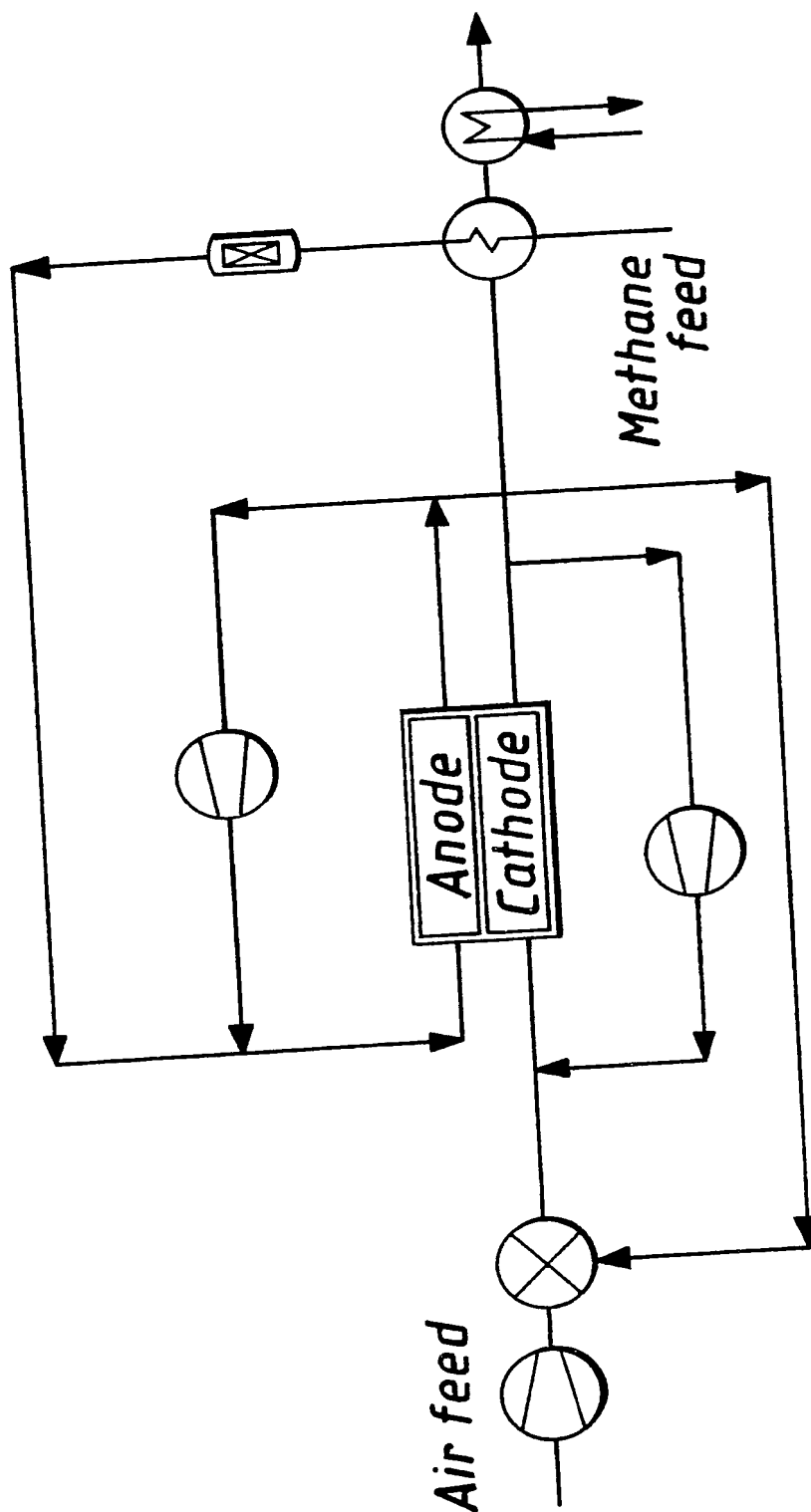
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FIG. 2.



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FIG. 3.



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A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 March 2003

Date of mailing of the international search report

28/03/2003

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Authorized officer

Besselmann, S

Continuation of Box I.2

Claims Nos.: 15-19

Claim 15 is vague and unclear in the sense that it does not contain any concrete technical feature which would allow the reader to define the scope of protection. Therefore no search of claim 15 is possible.

Claim 16 does not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The term "water dispersible solid solution" used in claim 16 has no well-recognised meaning and leaves the reader in doubt as to the technical feature to which it refers. Dependent claim 18 also throws doubt on the meaning of claim 16 since it describes the pH of the catalyst according to claim 16. However, claim 16 appears to define a solid material for which the pH is not generally defined. Furthermore, it is not clear whether claim 16 defines a catalyst or a washcoat comprising a catalyst.

For these reasons, claim 16 and dependent claims 17-19 lack clarity (and/or conciseness) within the meaning of Article 6 PCT to such an extent as to render a meaningful search of the claims impossible.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 02/04727

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 15-19
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04727

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